

III.A.31 Electrically Conductive, Corrosion-Resistant Coatings through Defect Chemistry for Metallic Interconnects

Objectives

- To synthesize and characterize coating materials with ultra-low oxygen diffusion coefficient, that are electronically conductive using site-specific doping and through fundamental understanding of defect chemistry, for application on metallic interconnect in intermediate temperature (800°C) solid oxide fuel cells (SOFCs).
- To apply the coatings on low thermal expansion, relatively inexpensive stainless steels and other alloys, and investigate oxidation kinetics in air and fuel atmospheres.
- To conduct a preliminary short stack (4-cell) test, using 5 cm x 5 cm active area cells to validate ex-situ results.
- To initiate work on the development of low-cost processes for the deposition of coatings on metallic interconnects.
- To offer coated interconnect foils to SECA vertical teams under suitable confidentiality agreements.

Approach

- Conduct literature search on the identification of suitable perovskite and nonperovskite materials exhibiting high electronic conductivity but very low oxygen ion conductivity. Non-perovskite materials of interest include spinels and bronzes.
- Synthesize perovskite oxides with transition element on the B-site, with site-specific doping to suppress oxygen vacancy concentration.
- Fabricate sintered bars and discs of the materials. Sintered bars are to be used for the measurement of total conductivity as a function of temperature. Discs are to be used for measuring ionic conductivity using electron blocking electrodes.

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- Deposit thin coatings of the materials on stainless steels and nickel-based alloy foils, and investigate oxidation kinetics.
- Conduct theoretical analysis of oxidation kinetics of coated and pristine alloys.
- Develop a method for the measurement of area specific resistance (ASR), and apply it to the foils oxidized under various conditions.

Accomplishments

- Identified a number of materials with low oxygen ion conductivity (possibly lower than 10^{-7} S/cm at 800°C) by taking into account ionic size effect.
- Fabricated LaMnO_3 and LaCrO_3 -based materials with dopant levels as high as 20% on the B-site to suppress oxygen ion conductivity.
- Measured total conductivity over a temperature range from room temperature to 800°C; and measured oxygen ion conductivity at 800°C.
- Sputter-deposited 1 and 3 micron coatings of various materials on Haynes 230, Inconel 718, and SS 430.
- Conducted oxidation studies in air up to 180 days at 800°C for samples having a LaMnO_3 based coating.
- Conducted oxidation studies in flowing 10% H_2 /90% N_2 gas with 5% humidity up to 90 days for samples having a LaCrO_3 coating.
- Examined oxide scale formed and measured its thickness on coated and pristine materials for oxidation times up to 180 days.
- Developed a theoretical model for oxidation kinetics and the experimental oxidation thickness data was verified with this model.
- Measured total ASR of the coated and pristine samples after oxidation for 45 days at 800°C. It was observed that the pristine samples exhibited significant oxidation. However, even samples with as small as 1 micron coating were highly resistant to oxidation.
- Carried out dip coating of LaMnO_3 based coatings on SS430 foils.

Future Directions

- Conduct a short stack test with the best coating material, as determined by ex situ oxidation studies.
- Conduct Hebb-Wagner measurements on YSZ/perovskite/YSZ sandwiches made by tape-casting.

Introduction

Planar SOFC stacks are preferred over their tubular counterpart due to compact design, higher power and energy density, and projected lower cost. However, planar SOFC stacks require interconnect or bipolar plates which keep fuel and oxidants separate, and electrically connect adjacent cells. From the standpoint of cost and ruggedness, metallic interconnects are preferred. However, metallic interconnects of choice are stainless steels or nickel-chromium-based alloys, which are prone to oxidation. The oxide scale formed increases the ASR, which adversely affects the SOFC performance and efficiency, and thus in balance also adversely affects the cost. The potential remedy is the development of either baseline alloys that are oxidation-resistant, or suitable coating materials which can suppress oxidation kinetics. From the standpoint of cost and practicality, the preferred approach is the development of suitable coating materials.

To date, several coating materials have been tried, with varying degrees of success. The approach, however, has not been systematic, and has relied on trial and error. As a result, most of the coatings used to date were very thick (several or several tens of microns). This increases the potential for spalling, which is undesirable. The approach selected in this work is based on the fundamental chemistry of materials, which has the potential to develop coatings that are adherent and very thin (typically less than 5 microns, and may be as thin as 1 micron), and yet can suppress oxidation kinetics to greater than 40,000 hours of operating life.

Approach

Possible coating materials are perovskites with a transition metal, capable of exhibiting multiple valence states. An example is LaMnO_3 . The approach involves doping a material such as LaMnO_3 (LM) with suitable elements, which tend to suppress oxygen vacancy concentration, without significantly reducing electronic defect concentration. Powders of various coating materials, doped appropriately, are made. Samples of the materials are made by sintering. Two types of electrical tests are performed: (a) measurement of total electrical conductivity; (b) measurement of oxygen ion conductivity using blocking electrodes. Thin coatings (1 to 5 microns) are then deposited on foils of various alloys. For the initial investigation, Haynes 230, Inconel 718, and SS 430 were the alloys selected. The coated and uncoated foils are subjected to air and fuel, for various periods of time and over a range of temperatures, up to $\sim 800^\circ\text{C}$. Samples are oxidized for various periods of time, up to a maximum of six months. The oxide

scale thickness is measured using scanning electron microscopy (SEM). The observed kinetics of oxidation is compared with the theoretical models developed. The ASR of the samples is also measured as a function of time of oxidation, with measurements conducted over a range of temperatures. Finally, a short stack will be tested using coated interconnects exhibiting the best properties.

Results

1. Identified a number of possible perovskite and non-perovskite materials with potential for good electronic conductivity and low oxygen ion conductivity. This was achieved using crystal chemistry considerations. Criteria based on ionic size were used to identify materials with low oxygen vacancy mobility. Criteria based on defect chemistry were used to identify materials with low oxygen vacancy concentration.
2. Samples of perovskite and non-perovskite structures were fabricated in the form of discs and bars. Total electrical conductivity, which is mainly electronic, was measured over a range of temperatures using the four probe DC method. Figure 1 shows the total conductivity measured as a function of temperature (Arrhenius plot) on several prospective coating

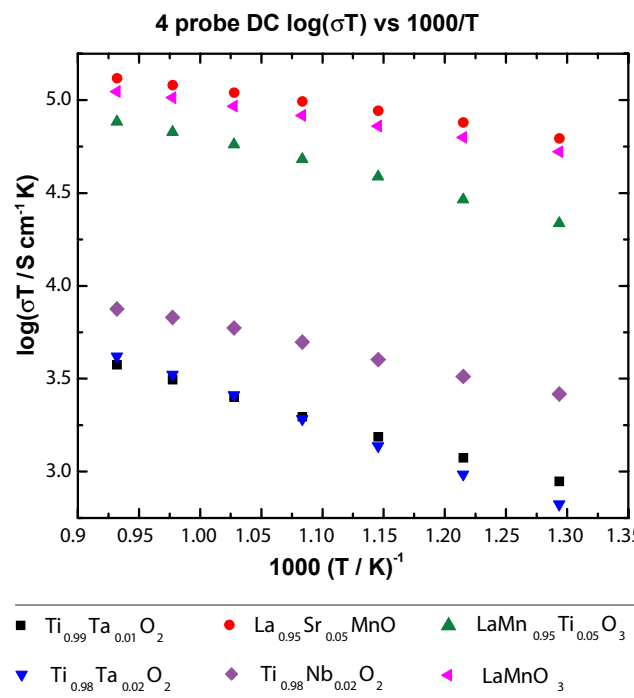


FIGURE 1. Arrhenius plots of conductivity of a number of coating materials. The total conductivity is predominantly electronic, with oxygen ion conductivity orders of magnitude lower.

- materials. The lowest measured value was ~ 4 S/cm, which shows that the ASR is expected to be low using any one of the coatings. Thus, the one with the lowest oxygen ion conductivity is preferred since this will be the most effective in suppressing oxidation kinetics.
- Experiments were conducted on the measurement of oxygen ion conductivity using blocking electrodes at 800°C . Results showed that the blocking electrodes function successfully. It was decided to use a three electrode configuration (with guard electrode) to eliminate the effects of surface conductivity. Lower values of conductivity were obtained for the sputter coated YSZ/perovskite couple as compared to the co-pressed sandwich structure. This was attributed to better equilibration to steady state in the thinner (sputter deposited) samples. The lowest value of conductivity was $2.0 \times 10^{-7} \text{ Scm}^{-1}$ and was obtained for titanium-doped LaMnO_3 (LMT). Experiments are under way to carry out measurements on tape-cast YSZ/perovskite/YSZ sandwich structures which will have stronger interfaces and thinner YSZ layers.
 - Successfully deposited a number of coating materials on several alloy foils. The thickness of the coating was varied between 1 and 3 microns.
 - Oxidation in flowing air was conducted at 800°C on the coated metal foils (LM, LMT and LSM) for durations up to 4,320 hours (180 days). The oxidized samples were characterized by XRD and SEM. The oxidation products were identified and the oxidation kinetics ascertained by measuring the thickness of the oxide layer as a function of time. The results demonstrated that the LMT coating was the most effective and strontium-doped LaMnO_3 (LSM) least effective in suppressing the oxidation kinetics of the alloys (Figures 2 and 3). The results were verified by a theoretical model and demonstrated that the LMT coating was the most protective.
 - Oxidation in flowing 10% H_2 /90% N_2 gas with 5% humidity was conducted on the coated metal foils (LaCrO_3 and Nb-doped LaCrO_3) for durations up to 2,160 hours (90 days). The oxide layer thickness was determined as a function of time. A 1 μm thick LaCrO_3 based coating was effective in decreasing the oxidation kinetics by more than an order of magnitude.
 - A spring loaded fixture was used to measure the ASR of the oxidized foils. Conductive paste was not used for these measurements as this could permeate the porous oxide layer and lead to an under-estimation of the ASR value. The ASR of the coated

Coated and uncoated metal foils oxidized in air at 800°C For 45 days.

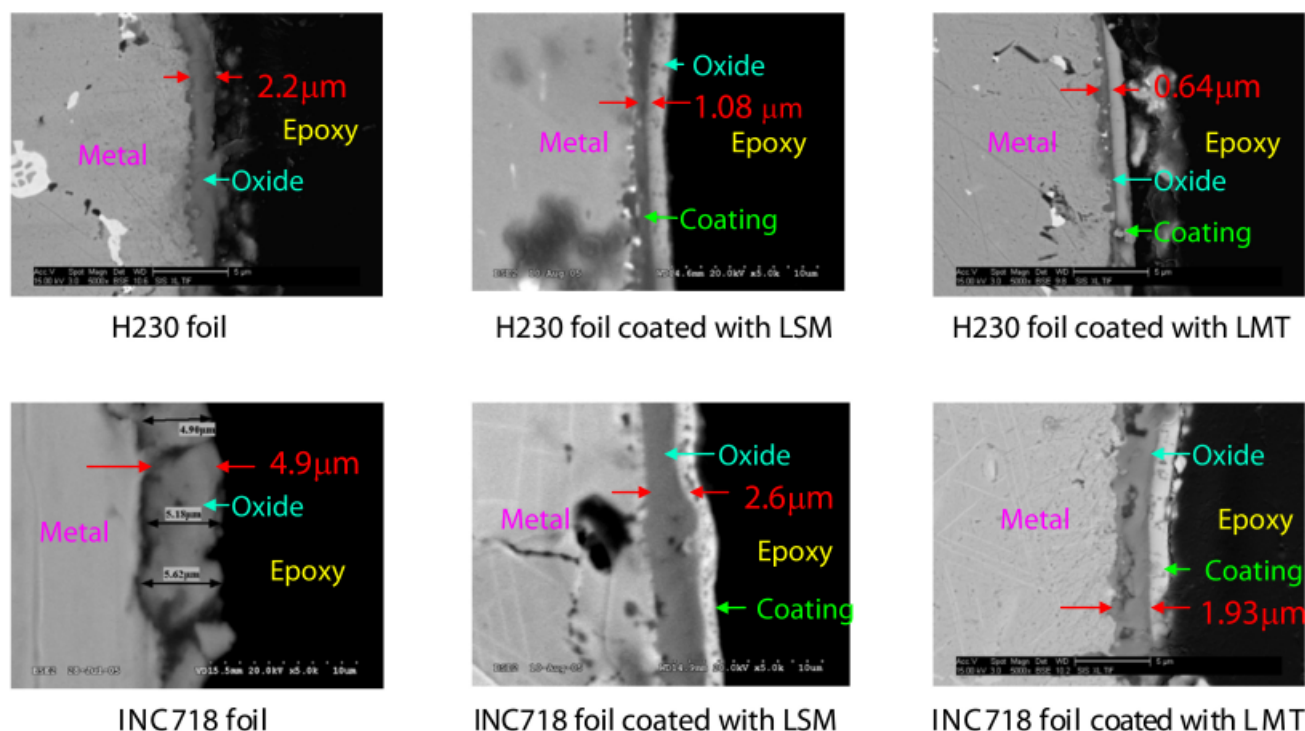


FIGURE 2. Cross sectional SEM micrographs of coated and uncoated metal foils oxidized at 800°C in air for 45 days. The thickness of the oxide layer is smaller for LMT coated foils as compared to LSM coated foils for H230 as well as INC718.

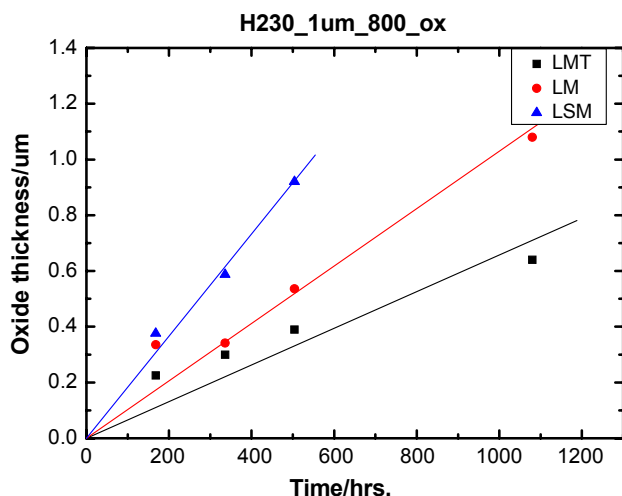


FIGURE 3. Graphical representation of the growth of oxide layer for H230 foil coated with LSM, LM and LMT and oxidized in air for 45 days (1,080 hrs.) at 800°C. The lowest slope for the LMT coated specimen is a validation of the defect chemistry approach.

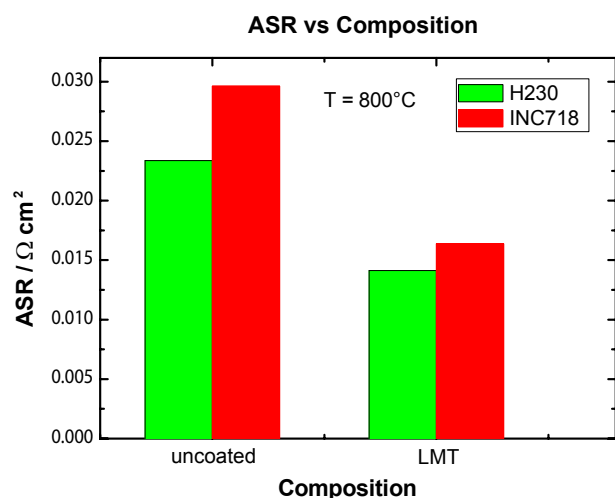


FIGURE 4. Comparison of ASR of uncoated and LMT coated foils of H230 and INC718, oxidized in air for 45 days at 800°C.

foils was compared with that of the uncoated foils. The ASR on the coated (1 micron) and uncoated foils showed that after 1,080 hours (45 days) in air at 800°C, the ASR of the coated foils was typically smaller by about half (Figure 4).

8. LSM and LMT were dip coated on to 2" x 2" SS430 foils. The coatings were cured at 1,000°C for 1 to 5 hours. The samples were characterized by SEM. The coatings were about 5 to 10 μm thick and showed excellent adherence.

Conclusions

1. Defect chemistry plays a major role in oxygen ion transport through oxides, and thus determines the suitability of a given material as a coating. Coating materials based on LaMnO_3 (perovskite) and TiO_2 (non-perovskite) were successfully made. It was demonstrated that perovskite coating is an order of magnitude superior to spinel coating.
2. Electronic and ionic conductivities of coating materials are in accord with defect chemistry, and that defect chemistry provides a scientific basis for the design of oxidation-resistant coatings.
3. High quality, strongly adherent coatings can be sputter deposited. The resulting foils exhibit improved oxidation resistance over the baseline foils. Even after several days at 800°C, the coating continues to remain well-bonded.
4. Coated foils also exhibit much lower ASR as compared to pristine foils.